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Local lattice structure, crystal field and energy level patterns in $CsCdBr_3:Tm^{3+}$ crystals

J. Heber[a,*], M. Lange[a], M. Altwein[a], B.Z. Malkin[b], M.P. Rodionova[b]

[a]*Technical University of Darmstadt, D-64289 Darmstadt, Germany*
[b]*Kazan State University, Kazan 420008, Russian Federation*

Abstract

In $CsCdBr_3$, Tm^{3+} substitutes for Cd^{2+}. It predominately forms symmetric dimer centers and single-ion centers, both of trigonal symmetry. The energy level schemes of both centers were determined by EPR and site-selective laser spectroscopy. To describe the spectra term dependent crystal-field parameters were deduced on the basis of a microscopic model taking into account the local lattice deformation induced by the impurity centers and the quasi-resonant virtual scattering of intrinsic lattice excitations by the Tm^{3+} ions.

Keywords: Crystal field; $CsCdBr_3:Tm^{3+}$; Local lattice deformation

1. Introduction

Dopant trivalent rare earth (RE) ions substitute for Cd^{2+} ions in the quasi-one-dimensional double bromides $CsCdBr_3$ forming optical centers with various mechanisms of charge compensation. Symmetric dimer centers, where the excess positive charge of a pair of RE^{3+} ions is compensated by a Cd^{2+} vacancy between them, are preferentially formed. Due to the close proximity of the optically active ions in the dimers these crystals are studied extensively as promising materials for up-conversion lasers [1,2]. In particular, efficient energy-transfer processes were observed in $CsCdBr_3$ codoped with Ho and Tm [3], and Pr and Tm [4]. Although the spectral properties of $CsCdBr_3$ crystals activated by different RE^{3+} ions have been thoroughly studied [5–7], the identification of the spectral lines with specific impurity centers still has a hypothetical character. A microscopic theoretical description of the splittings of the RE^{3+} states in the crystal field does not yet exist, and the mechanisms of the ion–lattice interaction and quantum up-conversion are not yet elucidated.

In this paper the energy levels of the two dominating optical centers with different charge compensation have been obtained by site-selective laser spectroscopy. By comparing the crystal-field splitting of the ground state $^3H_6$ with the results of the EPR measurements [8] we identify unambiguously one of the energy level schemes as belonging to the symmetric dimer center Tm^{3+}–Cd^{2+} vacancy–Tm^{3+} which substitutes for three adjacent Cd^{2+} ions in the linear chain of confacial $(CdBr_6)^{4-}$ octahedra. The distorted local structure of the crystal lattice around the isolated symmetric dimer is determined in a quasi-molecular model for the impurity center. The obtained inter-ionic distances were used to find an initial set of crystal-field parameters using the exchange charge model. These parameters were refined by a least-square fit to the experimental data of the crystal-field and Zeeman splittings.

We present here also the energy level scheme for one of the Tm^{3+} single-ion centers of C_{3v} symmetry (which may be of the type Tm^{3+}–Cd^{2+} vacancy–Cd^{2+}–Tm^{3+}) with energies only slightly different from those of the symmetric dimer. The absence of a second Tm^{3+} ion in the nearest neighbourhood of this center is confirmed by EPR experiments [8]. Analysis of the optical spectra has shown that the crystal-field parameters of the Tm^{3+} ions in the dimer and single-ion centers are strongly term-dependent. We assume that the observed selective increase of the crystal field, particularly affecting the Tm^{3+} ion in the $^1G_4$ state which is positioned in the gap between the lowest intrinsic absorption and emission bands of the host lattice, is caused by quasi-resonant virtual scattering of lattice excitons; a

*Corresponding author. Tel.: +49 6151 162483; fax: +49 6151 164883; e-mail: elpo@hrz1.hrz.th-darmstadt.de

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